

RETICULATED VITREOUS CARBON ELECTRODES FOR GAS PHASE PULSED CORONA REACTORS

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Abstract - A new design for gas phase pulsed corona reactors incorporating reticulated vitreous carbon electrodes is demonstrated to be effective for the removal of nitrogen oxides from synthetic air mixtures. The reactor consists of a plexiglass tube with porous reticulated carbon disk electrodes placed perpendicularly to the cylinder axis. Streamers propagate between the reticulated carbon disks providing a uniform exposure of the flowing gas stream to the electrical discharge. This mode of operation allows for convenient reactor scale-up and staging while maintaining the inter-electrode spacing in a moderate range, thus precluding the need for higher voltage power supplies. It is further envisioned that the reactor can be operated with multiple sets of electrodes placed in series down the length of the reactor in order to facilitate high efficiency removal of air pollutants.

Initial experiments with nitrogen oxide (NO) mixed in dry synthetic air at room temperature and pressure shows that the NO, as expected in an oxidizing environment, is converted to nitrogen dioxide with pulsed corona treatment. Most remarkable, however, is that for the higher operating voltages (55 and 61 kV) and longer residence times (above 24 sec.) the nitrogen dioxide and total NO_x, even in dry air, was reduced.

I. INTRODUCTION

Gas phase pulsed corona reactors have been extensively used and developed for the degradation and removal of many air pollutants including nitrogen oxides (NO, NO₂) [1]-[4], sulfur dioxide (SO₂) [5],[6], and volatile organic compounds (e.g., trichloroethylene, benzene, and toluene) [7] - [10] from a range of combustion gases and other gaseous waste streams. A pulsed corona reactor utilizes a high voltage pulsed electric field to create chemically reactive radicals, ions, and molecular species that in turn lead to the partial or complete degradation or conversion to less harmful byproducts of many pollutants. A pulsed streamer corona discharge creates streamer channels that propagate from one electrode to the other and that typically have relatively small diameter and very high tip electric fields.

One of the major difficulties in the design, construction, and operation of full scale pulsed corona

reactors is the scale-up from small laboratory units to large industrial units. Laboratory scale reactors have conventionally been designed using a wire-cylinder electrode geometry whereby a central wire serving as a high voltage electrode is suspended co-axially within a larger grounded cylindrical tube [5]. Scale-up is difficult due to the limitations of the gap spacing between electrodes; as the inter-electrode gap increases, the applied voltage needed to produce streamers completely filling the reactor increases, and the intensity and quality of the streamers formed decrease. Other electrode geometries, including point-plane and hollow tubes have been used [4], and these systems are also difficult to scale-up since single point electrodes do not provide a sufficient density of streamers for efficient waste removal.

The present work utilizes a fundamentally different type of electrode configuration to create streamers in the corona reactor [11]. A commercially available material made of reticulated vitreous carbon (RVC) [12], which has been used previously for low voltage electrochemical systems because of its high surface area and good electrical conductivity, is utilized in the present study for both high voltage and ground electrodes in the pulsed corona reactor. Reticulated vitreous carbon can be manufactured in a number of different shapes and configurations, and therefore can be readily adapted to the needs of pulsed corona reactors.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

In the present study a series of porous RVC disks is placed perpendicularly to the main axis of an outer insulated reactor cylinder as shown in Fig. 1. The corona discharge occurs at the surface of one RVC disk connected to a high voltage pulsed power supply and the streamers propagate toward the surface of another RVC disk placed several cm away and connected to a ground (Fig. 2). Because the discharge occurs from one disk to

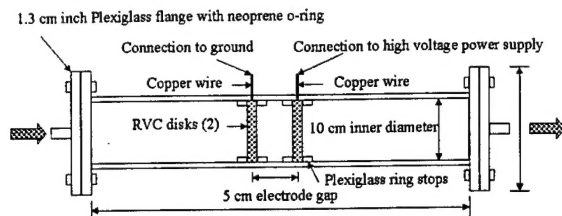


Fig. 1. Schematic of Reticulated Vitreous Electrode Corona Reactor

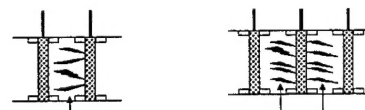
the other, the *diameter* of the reactor can, in principle, be very large while maintaining reasonable spacing between the electrodes. Since the electrodes are highly porous, the gas can flow through the electrodes and can contact the streamers very effectively. This is a fundamental advantage over the wire-cylinder geometry where the inter-electrode spacing limits the practical diameter of the reactor. Larger diameter reactors facilitate the treatment of larger volumes of gases. Several stages of RVC electrodes with alternating polarity could also be placed in a reactor creating multiple regions of corona discharge in a stepped approach to gas treatment.

Fig. 2 illustrates schematically the streamer propagation in the inter-electrode gap space for both the two and three electrode configurations. There is no fundamental limit to the number of such electrode sets that can be placed in series down the axis of the reactor. Furthermore, the various electrode sets can, in principle, be controlled at different voltage levels in order to potentially tune or optimize the reactor for a given application.

The reactor used in this study (Fig. 1) is a 10 cm (4 inch) inside diameter plexiglass tube with two or three RVC electrodes spaced 5 cm apart. Circular RVC disks approximately 1.3 cm ($\frac{1}{2}$ inch) thick and 10 cm in diameter were custom made by Electrosynthesis Company, Inc. (Lancaster, NY) and placed inside the 10 cm (4 inch) diameter tube. Two reactor configurations were studied. The first configuration consisted of two disks placed in series separated by a 5 cm gap with the high voltage lead attached to one disk and the ground lead attached to the other. The second configuration consisted of three RVC disks placed in series separated by 5 cm gaps with the high voltage lead attached to the center electrode and the ground leads attached to both of the end electrodes.

The active treatment volumes for the two configurations given above were 400 and 800 cm³, respectively. Nitric oxide at 100 ppm in a room

Two electrode configuration Three electrode configuration.



Active corona regions (streamer propagation)

Fig. 2. Schematic of Electrode Configuration and Streamer Propagation in RVC Corona Reactor.

temperature dry air stream was fed into the pulsed corona reactor at various flow rates to give residence times in the active zone of the reactor in the range of 7 to 50 seconds. The measured humidity of the feed gas was 0.0 % relative humidity at 25 °C. The outlet concentrations of NO and NO₂ were measured using a NO_x monitor (ThermoEnvironmental Instruments, Inc., Franklin, MA - Model 42H). Humidity and temperature were measured using a Cole Parmer TriSense velocity-temperature-humidity measurement system.

The high voltage power supply used in the present study is equivalent to that used in previous research [5],[6],[13]. Voltage and current waveforms were measured using a Tektronix TDS 460 fast digital storage oscilloscope with P6015A 1000x 3.0 pF, 1000 M Ω high voltage probe and a TCP202 15 A AC/DC current probe. The Wavestar program from Tektronix was used to collect the current and voltage data from the oscilloscope and place them in Excel files on a personal computer where integration was performed using Simpson's rule to obtain the power. The voltage was measured by attaching the probe to the high voltage electrode lead entering the reactor, and the current probe was placed on the ground wire at the outlet of the reactor.

III. RESULTS

The voltage and current characteristics of the gas phase RVC pulsed corona reactor were studied. Example current and voltage waveforms are shown in Fig. 3 and Fig. 4, and these figures indicate the fast rise time and exponential decay with some ringing that is typical in pulsed corona reactors with a rotating spark gap and wire cylinder electrodes [5], [6], [13].

The effects of RVC electrode arrangement on voltage rise time are shown in Fig. 5. Both electrode configurations had similar voltage rise times of about 25

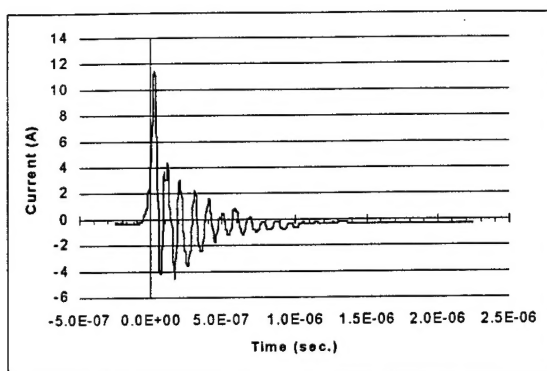


Fig. 3 Current waveform for reactor with the 3 - electrode configuration.

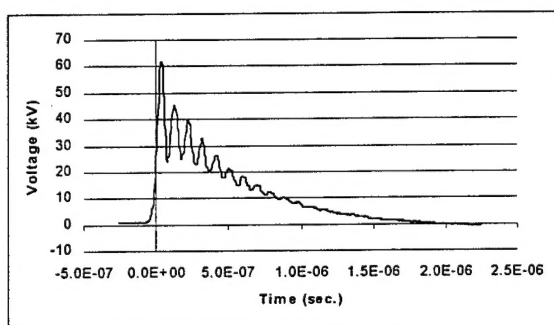


Fig. 4. Voltage waveform for reactor with the 3- electrode configuration.

ns for applied voltages up to 57 kV. Above this voltage level the rise time for the 3-electrode configuration increased to about 37 ns at 60 kV while the 2-electrode configuration showed no change in rise time.

Fig. 6 shows the effects of RVC electrode arrangement on peak current. For configuration 1 (the 2 - electrode design) the current is approximately 6 A at 50 kV and increases slowly to 7 A at 63 kV. Configuration 2 (the 3 - electrode design) gives a peak current approximately 10 - 13 A for peak voltages from 48 to 60 kV.

Fig. 7 shows the effect of peak voltage on the power for the two configurations. The power ranged from about 12 mJ/pulse to 30 mJ/pulse for the 3-electrode configuration and from about 12 mJ/pulse to about 20 mJ/pulse for the 2-electrode configuration as peak voltage ranged from 49 to 62 kV.

NO removal in the RVC reactor with the 3 - electrode configuration for various peak voltages as a function of residence time is shown in Fig. 8. For the two lower voltages (48 kV and 55 kV) the NO removal increased approximately linearly with residence time from 20 to 50 seconds, and at the higher voltage (61 kV) the NO removal was essentially complete for residence times above 24 sec. At 61 kV the energy cost for removing all of the NO_x at the 50 sec residence time

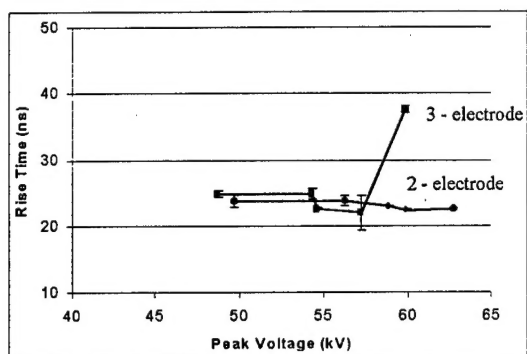


Fig. 5. Voltage rise time for both reactor configurations.

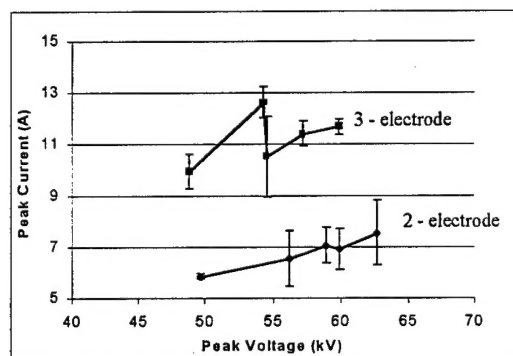


Fig. 6. Peak current for both reactor configurations.

was approximately 300 eV/NO or about 400 eV/ NO_x . The value for NO removal compares very well with literature values for NO removal in N_2 with 9% O_2 and 0.6% H_2O [14].

Fig. 9 shows the NO_2 concentration corresponding to the same experiments shown in Fig. 8. This figure shows the NO_2 concentration for the lowest voltage (48 kV) to increase with residence time. The intermediate voltage (55 kV) showed a continual decrease from 75 ppm to 60 ppm with residence time. The highest voltage showed a slight increase of NO_2 from 20 to 24 seconds followed by a decrease with residence time to 48 sec. These results indicate that the highest voltages (55 kV and 61 kV) were able to degrade both the NO and the NO_2 .

Fig. 10 shows the total NO_x concentration with time for the 3 - electrode configuration reactor. At the 48 kV voltage condition total NO_x increased slightly with residence time. The 55 kV and 61 kV experiments showed a reduction in total NO_x with residence time. This result is quite remarkable since total NO_x is very difficult to reduce in an atmosphere of dry air.

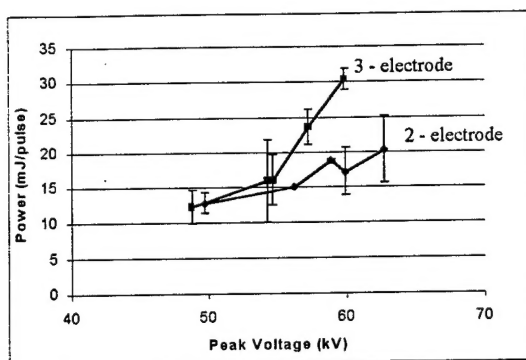


Fig. 7. Power per pulse for both electrode configurations.

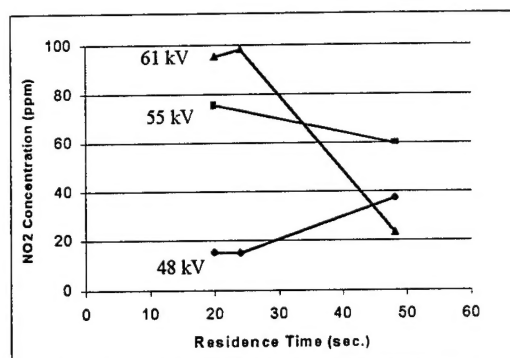


Fig. 9. NO₂ concentration for 3 - electrode reactor.

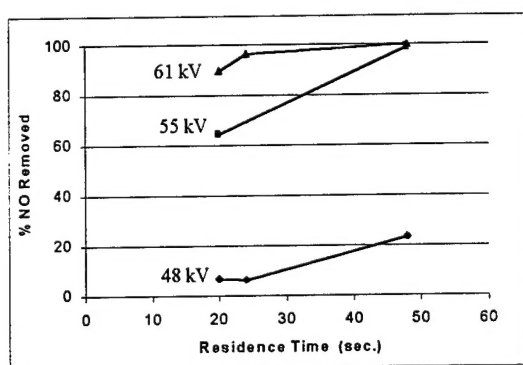


Fig. 8. NO removal for various peak voltages in 3 - electrode reactor.

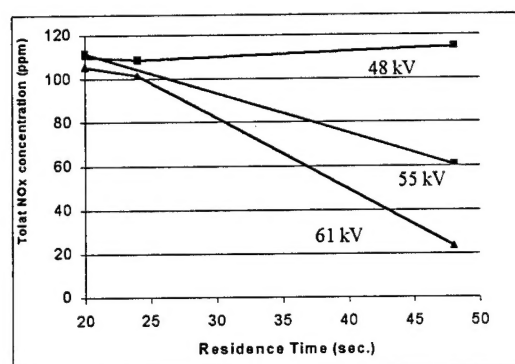
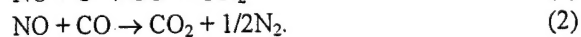


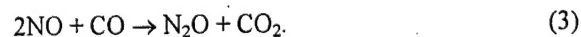
Fig. 10. Total NO_x concentration for 3 - electrode reactor.

IV. DISCUSSION

It is usually necessary to add water vapor to an atmosphere containing significant levels of oxygen in order to reduce total NO_x by pulsed corona, however, in the present system total NO_x decreased without the addition of water. Carbon is known to react with nitric oxide to produce molecular nitrogen and carbon dioxide through reactions [15,16]



It is also possible that small amounts of N₂O are formed by the reaction



Preliminary measurements with GC/MS indicate a possible small amount of N₂O formation in the RVC reactor. Reactions (1) and (2) generally occur at very high temperatures and have been demonstrated to remove up to 5000 ppm of NO at 700 °C [15].

It is possible that the above reactions may be

occurring in the pulsed corona reactor since electron energies near the electrode surfaces may be very high, however, further work is needed to measure the formation of carbon dioxide and the conversion of NO to molecular nitrogen. Experiments with ¹⁵N labeled NO have been conducted in conventional corona reactors in an atmosphere of dry nitrogen [17] and in various atmospheres with electron beam processes [18], and these methods would be useful to determine the reaction pathways in the present reactor.

Selective catalytic reduction using ammonia on pre-treated activated carbon has also been attempted, which showed that treating the activated carbon with aqueous solutions of ammonium sulfate and sulfuric acid was very effective in enhancing NO removal [19]. The interaction of NO₂ on carbon particles has also been considered and has been shown to lead to the reduction of NO₂ in dry and humid air [20]. In general, the major obstacle to the catalytic reduction of NO is that oxygen contained in the feed gas and released by NO decomposition competes with NO for adsorption sites and leads to catalytic poisoning [21]. Further work with the pulsed corona reactor is needed to assess the existence of these postulated reactions and to determine whether NO and NO₂ are reduced by the above mechanisms through

reactions with the carbon electrodes.

Recent studies have also shown that the adsorption of small chlorinated organic compounds on carbon can be enhanced by the application of low voltage (2-3 V) constant DC electric fields [22]. At these low voltages, the primary effect of the electric field was to lead to localized heating that in turn suppressed the adsorption of water, enhanced the oxidation of the organic, and served to regenerate the adsorbent. This suggests further work on the removal of gas phase organic chemicals using this reactor and electrode configuration. Current work is underway in our laboratory to address these issues.

V. CONCLUSIONS

The present work demonstrates that a pulsed corona reactor can be built and operated with reticulated vitreous carbon electrodes and that this reactor has fundamental advantages over other electrode configurations due to the relative ease of scale-up. In addition to the above factors, it has been demonstrated that RVC electrodes affect the chemistry of the induced corona reactions through possible chemically reductive processes, i.e., conversion of NO and NO₂ to N₂ and CO₂. Further tests are necessary to determine the ultimate fate of the nitrogen and to study the performance of the reactors with other gas compositions.

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REFERENCES

- [1] S. Masuda, S. Hosokawa, "Pulse energization system of electrostatic precipitator for retrofitting application," *IEEE Transactions on Industry Applications* vol. 24, p 708, 1988.
- [2] S. Masuda, H. Nakao, "Control of NO_x by positive and negative pulsed corona discharges," *IEEE Transactions on Industry Applications*, vol. 26, p 374, 1990.
- [3] J.S. Chang, P.A. Lawless, T. Yamamoto, "Corona discharge processes," *IEEE Transactions on Plasma Science*, vol. 19, p 1152, 1991.
- [4] T. Ohkubo, S. Kanazawa, Y. Nomoto, J.S. Chang, T. Adachi, "NO_x removal by a pipe with nozzle-plate electrode corona discharge system," *IEEE Transactions on Industry Applications* vol. 30, p 856, 1994.
- [5] A. Mizuno, J.S. Clements, "Methods for removing SO₂, NO_x, and particles from gas mixtures using streamer corona," United States Patent number 4,695,358, 1987.
- [6] J.S. Clements, A. Mizuno, W.C. Finney, R.H. Davis, "Combined removal of SO₂, NO_x, and fly ash from simulated flue gas using pulsed streamer corona," *IEEE Transactions on Industry Applications*, vol. 25, p 62, 1989.
- [7] T. Yamamoto, "VOC decomposition by non-thermal plasma processing - a new approach", *Proceedings of the IEJ-ESA 1996 Symposium on Electrostatics*, The University of Tokyo, Tokyo, Japan, pp 1-16, October 30-31, 1996.
- [8] T. Yamamoto, K. Ramanathan, P.A. Lawless, D.S. Ensor, J.R. Newsome, N. Plaks, G.H. Ramsey, "Control of volatile organic compounds by an ac energized ferroelectric pellet reactor and a pulsed corona reactor," *IEEE Transactions on Industry Applications*, vol. 28, p528, 1992.
- [9] T. Yamamoto, P.A. Lawless, M.K. Owen, D.S. Ensor, "Decomposition of volatile organic compounds by a packed-bed reactor and a pulsed-corona plasma reactor," *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Series, B.M. Penetrante and S.E. Schultheis, Eds. Berlin: Springer-Verlag, Vol. G34 Part B, p 223, 1993.
- [10] T. Yamamoto, K. Mizuno, I. Tamori, A. Ogata, M. Nifuku, M. Michalska, G. Prieto, "Catalysis-assisted plasma technology for carbon tetrachloride destruction," *IEEE Transactions on Industry Applications*, vol. 32, p 100, 1996.
- [11] B.R. Locke, "Reticulated vitreous carbon electrodes for reactor scale-up and enhanced removal of air pollutants in gas phase pulsed streamer corona," Provisional United States Patent, March 1998.
- [12] J. Wang, "Reticulated vitreous carbon - a new versatile electrode material," *Electrochimica Acta*, vol. 26, p 1721, 1981.
- [13] G. Sathiamoorthy, B.R. Locke, W.C. Finney, R.J. Clark, T. Yamamoto, "Halon Destruction in a Gas Phase Pulsed Streamer Corona Reactor", *Journal of Advanced Oxidation Technologies*, in press 1998.
- [14] M.A. Tas, *Plasma induced catalysis, a feasibility study and fundamentals*. Den Haag: CIP-Datat Koninklijke Bibliotheek, October 1995.
- [15] G. Bedyal, H.K. Orbach, F.C. Riesenfeld, "Reaction of nitric oxide with activated carbon and hydrogen," *Industrial and Engineering Chemistry*, vol. 50, pp 1165-1168, 1958.
- [16] D. Mehandjiev, E. Bekyarova, "Catalytic neutralization of NO on a carbon supported cobalt oxide catalyst," *J. Colloid and Interface Science*, vol. 166, pp 476-480, 1994.
- [17] B.R. Locke, R.J. Clark, G. Sathiamoorthy, W.C. Finney, "Reactions of isotopically labeled nitric oxide (N¹⁵O) in a gas phase corona reactor," *Proceedings of the NEDO symposium on non-thermal discharge plasma technology for air pollution control 1997*, December 22-23, 1997, Beppu Convention Bureau, Beppu, Japan and Kyushu Electric Power Company, Oita Branch Office, Oita, Japan, p 169, 1997.
- [18] O. Tokunaga, H. Namba, K. Hirota, "Experiments on chemical reactions in electron-beam-induced NO_x/SO₂ removal *Non-Thermal Plasma Techniques for Pollution Control*, NATO ASI Series, B.M. Penetrante and S.E. Schultheis, Eds. Berlin: Springer-Verlag, Vol. G34 Part B, p 55, 1993.
- [19] B.J. Ku, J.K. Lee, D. Park, H.-K. Rhee, "Treatment of activated carbon to enhance catalytic activity for reduction of nitric oxide with ammonia," *Industrial and Engineering Chemistry*, vol. 33, pp 2868-2874, 1994.
- [20] L.A. Gundel, N.S. Guyot-Sionnest, T. Novakov, "A study of the interactions of NO₂ with carbon particles," *Aerosol Science and Technology*, vol. 10, pp 343-351, 1989.
- [21] I. Masakazu, S. Hokoo, K. Sakai, S. Kagawa, "Catalytic decomposition of nitric oxide over copper(II)-exchanged Y-Type zeolites," *J. Chem. Soc., Faraday Trans. vol. 77*, pp 1629-1638, 1981.
- [22] E.G. Marchand, *Adsorption and catalysis on carbonaceous adsorbents: electronic factors*, Ph.D. Dissertation, Michigan Technological University, UMI, Ann Arbor, MI, 1996.